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Original Article

SYNTHESIS OF CYANINE DYES CONTAINING QUINOLINIUM HALIDE AND INVESTIGATION OF FLUORESCENCE PROPERTIES

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ABSTRACT

In this study, seven synergists were prepared to improve the contrast ratio in blue color filters derived from cyanine by quenching fluorescence. Improving contrast ratio of LCD color filters, therefore, requires the use of the colorant that can quench the fluorescence without also influencing the color. The colorant must also to be soluble in commercial solvent and stable on typical thermal conditions in the manufacturing process. Four synergists, were prepared in this study, they had absorption maxima of approximately 570~620nm and quenched fluorescence by more than 24%. The synergists increased the contrast ratio by about 30%, due to effective quenching of the fluorescence from the blue color filter, without changing the chromaticity diagram values.

KEYWORDS: LCD Color Filters, Synthesis of Cyanine Dyes Containing Quinolinium Halide and Investigation

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INTRODUCTION

The contrast ratio is an important color property of liquid displays. Color properties, which are classified as purity, contrast ratio, and brightness, mainly depend on pigment properties. However, the blue color filter has an unexpected fluorescence in the wavelength of desired high transmission, caused by small amount of supplementary colorant. Effective improvement in the contrast ratio requires the use of synergists that have properties such as spectral compatibility when the absorbance spectrum of the quencher overlaps the emission spectrum of the fluorescence, high molar extinction coefficient and little influence on the color of the blue color filter. This study investigated the FRET(Foster resonance energy transfer) efficiency by measuring the fluorescence spectra of four colorants **1**-**4** derived from cyanine dye. The prepared dyes were used to examine the FRET process between synergists and colorants of the blue color filter that emitted fluorescence in the wavelength of the desired high transmission. The influence of the FRET process on the properties of LCD color filters with the synthetic synergists is also thoroughly discussed. The FRET efficiency was investigated using the measured fluorescence spectra, and the solubility, spectral and thermal properties of the synergists were examined. In addition, the transmittance, contrast ratio, and color difference values of spin-coated films containing the synthetic synergists were investigated.

EXPERIMENTAL

Synthesis of Colorants

Synthesis of 2, 3, 3-Trimethylindolenine(Intermediate 1): Aceic acid(20ml) was added to3-methyl-2-

butanone(4.09 g, 0. 047 mol) and the temperature were raised to 60℃. Subsequently, phenyl hydrazine(5.23 g, 0. 047 mol) was slowly added and the mixture was refluxed for 12 hours. After the reaction was terminated, water(20 mL) was added to the mixture and neutralized with sodium hydroxide. Ethyl acetate(15 mL) was added and the resulting mixture was extracted several times with ethyl acetate, followed by drying with $MgSO_4$(around 1 g) and filtration. Evaporation of the ethyl acetate gave a precipitated product.

Intermediate 1: Yield: 54%, ^{1}H NMR(400MHz, DMSO-d_6): 1.23(s, *6H*, CH_3), 1.94(s, *3H*, CH_3), 7.06(d, *1H*, CH), 7.30(t, *1H*, CH), 7.41(t, *1H*, CH), 7.45(d, *1H*, CH). EA: found C: 82.87 H:8.38 N:8.79 calculated for $C_{11}H_{13}N$ C:82.97 H:8.23 N:8.80, MS(*m/z*) 159(M+).

Synthesis Of1-Ethyl-2, 3, 3-Trimethyl-3*H*-Indolium Iodide(Intermediate 2): Intermediate**2(**0.5 g, 3.14 mmol) was dissolved in acetonitrile(2.5 mL), followed by the addition of 1-iodoethane(1.47 g, 09.42 mmol). The solution was refluxed with constant stirring for24 hours. The solvent was concentrated and removed under vacuum. The reaction mixture was cooled in an ice bath and solid was obtained upon addition of acetone. The resulting crystals were filtered and dried.

Intermediate **3** and **4** were synthesized in the same manner.

Intermediate 2: Yield : 70%, ^{1}H NMR(400MHz, DMSO-d_6) : 1.3(s, *6H*, CH_3), 1.6(m, *2H*, CH_2), 1.61(t, *3H*, CH_3), 1.69(s, *6H*, CH_3), 7.30(d, *1H*, CH), 7.37(t, *1H*, CH), 7.70(t, *1H*, CH), 7.92(d, *1H*, CH), EA : found C:49.87 H:5.38 N:4.79 calculated for $C_{13}H_{18}IN$ C:49.54 H:5.76 N:4.44, MS(*m/z*)315(M+).

Intermediate 3: Yield : 72%, ^{1}H NMR(400MHz, DMSO-d_6) :0.9(s, *3H*, CH_3), 1.2(m, *2H*, CH_2), 1.21(t, *3H*, CH_3), 1.29(s, *6H*, CH_3), 7.30(d, *1H*, CH), 7.37(t, *1H*, CH), 7.80(t, *1H*, CH), 7.93(d, *1H*, CH), EA : found C:66.87 H:6.38 N:4.79 calculated for $C_{19}H_{22}BrN$ C:66.28 H:6.44 N:4.07, MS(*m/z*) 344(M+).

Intermediate 4: Yield : 92%, ^{1}H NMR(400MHz, DMSO-d_6) :1.58(t, *3H*, CH_3), 2.59(s, *3H*, CH_3), 5.01(m, *2H*, CH_2), 8.01(m, *1H*, CH), 8.20(t, *1H*, CH), 8.33(t, *1H*, CH), 8.42(d, *1H*, CH), 8.61(d, *1H*, CH), 9.40(d, *1H*, CH), EA : found C:48.17 H:4.70 N:4.70 calculated for $C_{12}H_{14}IN$ C:48.18 H:4.72 N:4.68, MS(*m/z*)229(M+).

Synthesis of(E)-1-ethyl-4-(2-(phenylamino) vinyl) Quinolinium iodide(intermediate 5): Intermediate**4(**0.9 g, 3.14 mmol) and *N,N*-diphenyl methanimidamide(0.62g. 3.14mmol) were dissolved in acetic anhydride(2.5 mL).The solution was refluxed with constant stirring for 3 hours to produce a solution. The reaction mixture was cooled and a solid was obtained upon washing with ethyl ether. The resulting crystals were filtered and dried.

Intermediate 5: Yield : 44%, ^{1}H NMR(400MHz, DMSO-d_6) :1.59(t, *3H*, CH_3), 4.82(m, *2H*, CH_2), 6.14(s, *1H*, H), 6.89(t, *1H*, CH), 7.20(t, *2H*, CH), 7.26(d, *2H*, CH), 8.09(s, 2*H*, H), 8.10(t, *1H*, CH), 8.23(t, *1H*, CH), 8.42(d, *1H*, CH), 8.61(d, *1H*, CH), 9.01(d, *1H*, CH), 10.55(s, *1H*, H), EA : found C:56.70 H:4.98 N:6.76 calculated for $C_{19}H_{19}IN_2$ C:56.73 H:4.76 N:6.96, MS(*m/z*)402(M+).

Synthesis of 1-ethyl-4-((1E, 3E)-3-(1-ethyl-3, 3-dimethylindolin-2-ylidene)prop-1-enyl) quinolinium iodide(dye 1): Intermediate**2(**0.9 g, 3.14 mmol) and intermediate 5(0.62g. 3.14mmol) was dissolved in acetic anhydride(2.5 mL), followed by the addition of 1-iodoethane(1.47 g, 09.42 mmol). The solution was stirred for5 hours in 60℃.The reaction mixture was cooled and solid was obtained upon wash with ethyl ether. The resulting crystals were filtered and dried.

Intermediate **2-4** were synthesized in the same manner.

Synergist 5 : Yield : 47%, 1H NMR(400MHz, DMSO-d6) :1.32(t, 3H, CH3), 1.60(t, 3H, CH3), 1.71(s, 6H, CH3), 4.88(m, 2H, CH2), 4.91(m, 2H, CH2), 6.24(s, 1H, H), 6.25(d, 1H, CH), 7.08(t, 1H, CH), 7.11(s, 1H, H), 7.22(s, 1H, H), 7.35(t, 1H, CH), 7.58(d, 1H, CH), 7.89(d, 1H, CH), 8.10(t, 1H, CH), 8.23(t, 1H, CH), 8.32(d, 1H, CH), 8.61(d, 1H, CH), 8.65(d, 1H, CH), EA : found C:62.81 H:5.79 N:5.72 calculated for C26H29IN2 C:62.91 H:5.89 N:5.64, MS(m/z)496(M+).

Synergist 6 : Yield : 44%, 1H NMR(400MHz, DMSO-d6) :1.31(t, 3H, CH3), 1.58(t, 3H, CH3), 1.72(s, 6H, CH3), 4.87(m, 2H, CH2), 4.90(m, 2H, CH2), 6.21(s, 1H, H), 6.23(d, 1H, CH), 6.69(t, 1H, CH), 6.71(s, 1H, H), 6.81(s, 1H, H), 7.15(t, 1H, CH), 7.18(d, 1H, CH), 8.19(d, 1H, CH), 8.20(t, 1H, CH), 8.23(t, 1H, CH), 8.42(d, 1H, CH), 8.61(d, 1H, CH), 8.80(d, 1H, CH), EA : found C:60.65 H:5.48 N:5.72 calculated for C26H29F6N2PC:60.70 H:5.68 N:5.44, MS(m/z)514(100).

Synergist 7 : Yield : 42%, 1H NMR(400MHz, DMSO-d6) :1.48(m, 3H, CH3), 1.69(s, 6H, CH3), 3.06(t, 2H, CH2), 4.22(t, 2H, CH2), 4.71 (m, 2H, CH2), 6.11 (s, 1H, H), 6.23(d, 1H, CH), 6.65(t, 1H, CH), 6.71(s, 1H, H), 6.82 (s, 1H, H), 7.04 (t, 1H, CH), 7.08 (d, 1H, CH), 7.27 (t, 1H, CH), 7.31 (d, 2H, CH), 7.48 (t, 2H, CH), 8.09 (d, 1H, CH), 8.10 (t, 1H, CH), 8.23 (t, 1H, CH), 8.41 (d, 1H, CH), 8.71 (d, 1H, CH), 8.91 (d, 1H, CH), EA : found C:67.09 H:5.92 N:4.70 calculated for C32H33IN2 C:67.13 H:5.81 N:4.89, MS(m/z)572(100).

Synergist 8 : Yield : 38%, 1H NMR(400MHz, DMSO-d6) :1.49(t, 3H, CH3), 1.73(s, 6H, CH3), 3.16(t, 2H, CH2), 4.72(t, 2H, CH2), 4.81 (m, 2H, CH2), 5.64 (s, 1H, H), 6.24(d, 1H, CH), 6.69(t, 1H, CH), 6.73(s, 1H, H), 6.81 (s, 1H, H), 7.05 (t, 1H, CH), 7.08 (d, 1H, CH), 7.27 (t, 1H, CH), 7.29 (d, 2H, CH), 7.40 (t, 2H, CH), 8.11 (d, 1H, CH), 8.13 (t, 1H, CH), 8.25 (t, 1H, CH), 8.42 (d, 1H, CH), 8.61 (d, 1H, CH), 8.93 (d, 1H, CH), EA : found C:65.55 H:5.38 N:4.72 calculated for C32H33F6N2PC:65.08 H:5.63 N:4.74, MS(m/z)590(100).

Investigation of Solubility: The solubility of the synthesized colorants tested in propylene glycol methyl ether acetate(PGMEA), cyclohexanone, diemthylformamide(DMF) and diacetone alcohol(DAA). The prepared dyes were added to the solvents at various concentrations, and the solutions were sonicated for 5min using an ultrasonic cleaner(ME6500E). The solutions were left to stand for 48h at room temperature, and checked for precipitation as determination of the solubility of the dyes.

Structural Analysis: Structural analyses of synthesized dyes were conducted using an EA 1108(Elemental Analysis) and a Voyager-DE STR Biospectrometer(MALDI-TOF). UV-visible absorption spectra were obtained with a Shimadzu UV-2100 spectrophotometer. Fluorescence spectra were measured using a Scinco, Fluorinate FS-2 fluorescence spectrophotometer.

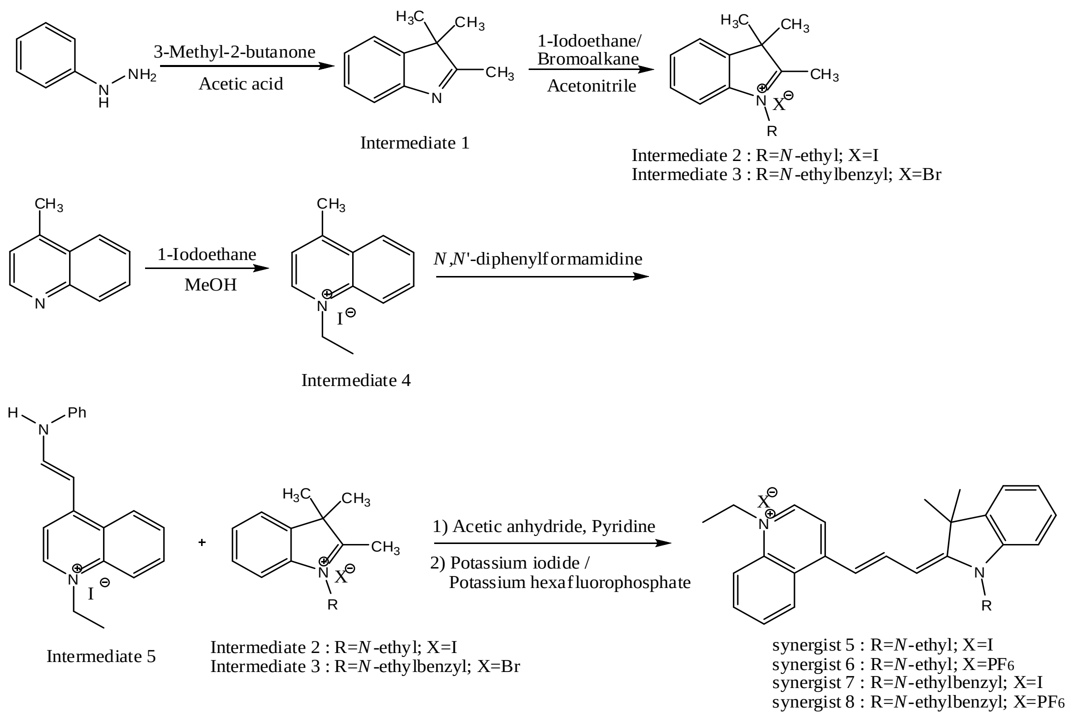

Figure 1: Synthetic Scheme of Synthesis of dyes(1-4)

Measurement of Spectral and Chromatic Properties

The spectral properties of Rhodamine Bare similar to those of the supplementary colorant of the blue color filter, so the spectral and chromatic properties of synthesized colorants **1**-**4** were compared with those of Rhodamine B. The absorption spectra of the synthesized colorants dissolved in DMF were measured using a HP 8452A spectrophotometer. Fluorescence spectra of Rhodamine B with the synthesized colorants, dissolved in DMF were measured using a Scinco, Fluorinate FS-2 fluorescence spectrophotometer.

Measurement of Thermal Stability

The thermal stability of the synthesized dyes was evaluated by thermogravimetry(TGA). The prepared dyes were heated to 110 ℃ and held at that temperature for 10min to remove the residual water and solvents. The dye was then, heated to 220 ℃ and held at that temperature for 30 min to simulate the thermal processing conditions of color filter manufacturing. The dyes were finally heated to 400 ℃ to determine their degradation temperature. The heating was carried out at the rate of 10 ℃/min under a nitrogen atmosphere.

Preparation of Color Filters

Spin-coating was carried out onto glass using a MIDAS System SPIN-1200D spin-coater. The glass was spun at a low to moderate speed of 300 rpm for 10 seconds to create an even spread of the solution. The solution was prepared with 2g of colorants(C.I. Pigment Blue 15:6 : Rhodamine B : colorant = 86:6:8), 3.5g of acrylic binder, 3.5g of dipentaerythritol penta/hexaacrylate, 0.5g of Ingacure-369 and 9.5g of DAA. Once spin-coating was completed, the film was placed quickly onto a hot plate(heated to around 100℃) for 5 minutes to evaporate the solvent, pre-baked at 90℃ for 90 seconds and post-baked at 220℃ for 40min. After each step, the transmittance spectra of the colorant-coated glasses were measured.

RESULTS & DISCUSSIONS

Solubility

For successful application in LCD color filters, colorants should exhibit high solubility in industrially used organic solvents, such as PGMEA, DAA. Regardless of the compatibility with binders formulated in the final color photo-resist, the colorant is acceptable when its solubility is more than 5 wt% in organic solvents and it exhibits the desired optical properties.

Organic compounds having high molecular weight are readily undergo intermolecular interactions, such as Vander Waals force and dipole-dipole interaction, which lead to low solubility. The solubility of colorants **1-4**, therefore, could be influenced by the types of quaternary ammonium salts and their molecular weights. All four colorants **1-4** showed incomparably higher solubility in DAA than in the other organic solvents. In this series, colorant **2**and **4** tended to have higher solubility particularly in DAA which indicated that bulky anion(hexafluorophosphate ion) lead to high solubility. Colorant 2 had a higher solubility than Colorant 4 which indicated that a small molecular weight lead to high solubility. Therefore the solubility of four colorants 1-4 was observed in decreasing order as DAA > cyclohexanone > PGMEA.

Thus, in terms of solubility, three colorants **2-4**were suitable for the fabrication of LCD color filter. The solubilitiesof four innovativesynthesized colorants **1-4** in some organic solvents are listed in Table 1.

Table 1: Solubility of Synthesized Colorants 1-4 in Different Solvents

	Solubility(wt %)		
	PGMEA	CHN	DAA
1	0	1	2
2	0	2	3
3	0	1	3
4	0	1	3

Characterization of the Spectral Properties of the Colorants

Solvatochromism can be best described as the effect of a solvent on the absorption maxima of a coloring material. Solvent-solute interactions have various influences on the absorption spectrum, such as the λ_{max} value and the band intensity. Generally, many dye molecules have a ground state that is less polar than the excited state so that a polar solvent will tend to stabilize the excited state more than the ground state, leading to a bath chromic shift in the absorption maximum. In contrast to this positive solvatochromism, negative solvatochromism is most often observed with colorants that contain a delocalized charge, such as cyanine colorants **1-4**.

The absorption maxima of synthesized colorants **1-4** were determined in various organic solvents as shown in Table 2. The absorption maxima of cyanine colorants **1-4** were in the range of 603-604 nm in DMF, whereas they were red shifted to 598-599 nm in $CHCl_3$ which clearly indicated a negative solvatochromism for the four cyanine colorants **1-4**. The absorption maxima of colorants **1-4** were very similar, indicating small effects on the absorption maximum by the *N*-alkyl substituent on the in dole nitrogen atom. Intermolecular hydrogen bonding between solvent and colorant molecule can also give rise to hypsochromic shifts, particularly in case of $n \rightarrow \pi^*$ bands. Accordingly, the excitation energy will be raised by the hydrogen bond, which stabilizes the n-electrons to give rise to a hypsochromic shift in the absorption spectrum. Therefore, the absorption maxima of colorants **1-4** exhibited hypsochromic shifts of around 2-3nm ethanol when compared to DMF. The molar extinction coefficients of colorants **1-4** ranged between 48,000 and 55,000 in DMF, colorant 1had the strongest maximal absorbance value, as shown in Table 2.

Table 2: Absorption Maxima of the Synthesized Colorants 1-4 in Different Solvents

Colorant Number	λ_{max}(nm)				
	Chloroform	Acetone	Ethanol	DMF	ε_{max}^{*} ($Lmol^{-1}cm^{-1}$)
Rhodamine B**	-	-	-	542	-
1	599	601	602	604	55,000
2	598	600	601	603	53,000
3	599	601	601	604	51,000
4	599	601	602	602	48,000

* ε_{max} determined in DMF

** Emission maximum of Rhodamine B: 570 nm in DMF

Improvement in the contrast ratio requires a FRET process to quench, the emission of fluorescence in blue color filter caused by supplementary pigment. FRET is one of the most common mechanisms of fluorescent quenching and can occur when the emission spectrum of the fluorescent donor overlaps the absorbance spectrum of the quencher and when the donor and quencher are within a sufficient distance known as the Foster distance.

In brief, FRET efficiency was calculated according to the following formula(1):[5]

$$E = 1 - \frac{I_{DA}}{I_D} \qquad (1)$$

Where, E is the FRET efficiency value

I_{DA} is the acceptor fluorescence intensity with donor excitation

I_D is the donor fluorescence intensity with donor excitation

In this study, the calculations of FRET efficiency were compared between the four colorants **1-4** and Rhodamine B which had very similar spectral properties to that of supplementary colorants used in the blue color filter, as summarized in Table 2. The practical FRET efficiency of colorants **1-4** was examined at diverse ratios with respect to the weight of Rhodamine B(25wt%, 50wt% and 75wt %), as summarized in Table 4. The FRET efficiency of colorants 1-4 was effective. Colorants **1-4**, therefore, caused an 83-87% reduction of fluorescence of Rhodamine B at 75wt% concentration, 75-78% reduction at 50wt%, and 43-45% reduction at 25wt%.

Table 3: Fret Efficiency of Colorants with Rhodamine B

Wt% of Colorant	1	2	3	4
0	0			
25	45	43	43	44
50	77	78	75	76
75	87	85	83	85

Characterization of Thermal Stabilities

Colorants synthesized for the fabrication of color filters require strict thermal stability to withstand the post baking process which is generally carried out at 210 ~ 220 ℃. Therefore the weight reduction of colorants should be as small as possible at 200 ~ 230 ℃, as determined by TGA.Table 4, show that, colorant **3** and **4**had better thermal stability, as they showed no weight loss at 230 ℃, and a weight loss of less than 1% at 250 ℃.By contrast, colorants**1** and **2** showed comparatively poor thermal stability, with weight loss in the range of 2.8 ~ 4.3% at 230 ℃. Therefore, high molecular

weight of the colorants would appear to be advantageous for thermal stability. The colorants synthesized in this study appear to be very suitable materials for use in fabrication of LCD color filters, particularly for blue pixels,due to their extremely high thermal-stability.

Table 4: Weight Reduction of Colorants 1-4 at Different Temperature Measured by TGA

Colorant Number	Weight(%)	
	200℃	230℃
1	98.63	95.75
2	99.30	96.05
3	97.63	93.55
4	99.12	96.55

Spectral and Chromatic Properties of Spin-Coated Color Filter

The coordinate values of the blue color filters spin-coated with synergists are summarized in Table **5**and compared to the blue color filter without synergists.

The chromaticity diagram of the blue color filter with synthesized synergists**1**and, **3** exhibited identical x, y values with those of the blue color filter. This indicated thatthe color shade of the blue color filter was retained in the presence of small amounts of the added synergists, about 5%. The Y value of the blue color filter with synergist 1 was 10.23, which was larger than that of the blue color filter. The Y value of the blue color filter with synergist 3 was 9.33, which was that of the blue color filter. The contrast ratio of the blue color filter after adding synergist 1 or 3 was significantly increased by approximately 10-25%, presented as 12465 and 10813 respectively. Synergists 1 and, 3 effectively quenched fluorescence which is a factor of the decreasing contrast ratio. Therefore, the absorption spectra of the synergists were suitable for improving the contrast ratio.

Table 5: Chromaticity Co-Ordinate(x,y,Y) and Contrast Ratio of the Blue Color Filter with Synthesized Synergists

Colorants Number	Chromaticity Co-Ordinates			Contrast Ratio
	x	y	Y	
Blur color filter	0.138	0.089	10.16	10076
1	0.138	0.088	10.18	12465
2	0.137	0.089	9.78	10813

CONCLUSIONS

In summary, among the four synthesized colorants, colorant **1** had limited solubility, whereas colorants **2-4** exhibited suitable solubility for use with color filters. The solubility of the colorants was related to the type of quaternary ammonium salts and their molecular weights. The absorption maxima of colorants **2-4** ranged from 550 ~ 567 nm in DMF and molar the extinction coefficients of colorants **2-4** were ranged between 70,000 and 92,000 in the same solvent. The FRET efficiency of colorants **1-4** was calculated to show that colorant **1**wouldoverlap the most with the emitted fluorescence of Rhodamine B. These calculated results were also supported by the percent reduction of fluorescence of Rhodamine B in solution. The weight losses of colorants, determined by TGA, indicated that colorants **3** and **4**were extremely stable during a heat treatment at 230 □, indicating the suitabilityof the synthesized colorants for improving the color properties of blue pixel.

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